Spectral properties of atoms in fields: A semiclassical analysis

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We develop a semiclassical theory for the spectral rigidity of nonhydrogenic Rydberg atoms in electric fields, and evaluate the significant deviations from the well-known Poissonian behavior in the hydrogenic case. The resulting formula is shown to be in excellent agreement with the exact quantal result. We also investigate diamagnetic atoms; we find that, in contrast to the classically integrable atoms, diffraction has a small effect on the spectral rigidity in the classically chaotic atom. We show that our predictions can also be of use in the mixed phase space regime.

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The short-range spectral properties of nonhydrogenic Rydberg atoms in external fields were recently found to have an unexpected character [1]: the nearest neighbor distribution was neither Poisson nor Wigner-Dyson, but close to a new generic *intermediate* class known as *half-Poisson*. These findings have been investigated experimentally for helium atoms in electric fields [2], following much interest in the dynamics of nonhydrogenic atoms in weak fields and the effects of *core-induced chaos* [3–7]. Concurrently, there has also been much interest in such intermediate nearest neighbor distributions [8,9], with broad application in problems such as electron-electron interactions in closed mesoscopic devices [9,10], the metal-insulator transition [11], intruder states in nuclear physics [12], and inclusions in billiards [8]. These studies of intermediate statistics have exclusively employed quantum calculations.

Here we obtain spectral rigidities of nonhydrogenic Rydberg atoms in electric and magnetic fields from an accurate quantal calculation. We find interesting and substantial deviations from Poissonian (hydrogenic) behavior in the integrable (electric field) and near integrable (weak magnetic field) cases. We develop a semiclassical theory for Stark spectra which is in good agreement with the quantal results, and show that one-scatter diffractive orbits account for most of the effect. In contrast we find a comparatively small effect in the case of fully chaotic Rydberg atoms. To our knowledge this is the first analysis of the curve form of the spectral rigidity for a generic atom, which we derive from classical dynamical information. Our semiclassical analysis should be extendable to the mixed phase space Kolmogorov-Arnold-Moser (KAM) case.

The spectral rigidity, defined as

$$\Delta(L) = \min_{A,B} \frac{\rho}{L} \int_{-L/2\rho}^{L/2\rho} de \langle [\mathcal{N}(E+e) - A - Be]^2 \rangle_E, \quad (1)$$

where $\mathcal{N}(E)$ is the spectral staircase function, ρ is the density of states (assumed constant over the range of L to be considered), and $\langle \cdots \rangle_E$ denotes averaging over the spectrum, was first analyzed semiclassically for classically integrable and chaotic systems by Berry [13]. It provides a measure of long-ranged deviations from the Weyl rule for spectral density, and for diffraction-free systems is controlled [for $L \gtrsim O(1)$] by classical dynamical correlations. For $L \lesssim O(1)$ it converges universally to the form $\Delta(L) = L/15$ for symmetry reduced spectra.

The hydrogen atom in a static electric field (of strength F) or in a magnetic field (of strength B) provided some of the *cleanest* illustrations of integrability, mixed phase space, and chaos in a real system [14]. The dynamics of the electron is two-dimensional and has a useful scaling property: the classical dynamics depends only on a scaled energy $\epsilon = E\kappa^2$, where $\kappa = F^{-1/4}$ for the electric field case and $\kappa = B^{-1/3}$ for the magnetic field case. This property is exploited in both experiment and theory. Spectra are obtained at fixed ϵ, and the corresponding eigenvalues κ_i represent effective values of $\hbar^{-1}$ with fixed classical dynamics. Hydrogen in a magnetic field is near integrable for $\epsilon < -0.5$; as the field is increased it makes a gradual transition to full chaos at $\epsilon \simeq -0.1$. The Hamiltonian for hydrogen in an electric field is always separable. We consider field values where the eigenvalues are well below the ionization threshold at $\epsilon = -2$, so the system may be considered integrable and bound.

Most experiments in fact investigate atoms other than hydrogen (typically He, Li, or Rb). The useful scaling property may still be exploited, but the inner core of electrons yields nontrivial effects: additional weak spectral modulations and spectral statistics near the Wigner-Dyson limit even for the integrable–near integrable regime [4–6]. Hence the interest in so-called *core-induced chaos*. The additional modulations are accurately described by diffractive periodic orbit theory [7,15]. An investigation [1] of the next nearest neighbor (NNS) statistics for the lowest 40 000 eigenvalues showed that they are only near the Wigner-Dyson limit for the lowest ~1000 states. For small $\hbar$ they were found to make a transition to an intermediate distribution $P(s) \sim \alpha s e^{-2s}$ with $(\alpha \sim 3-4)$, near to the half-Poisson distribution (for which $\alpha = 4$).

Rydberg atoms and molecules are well described by quantum defect theory, one of the most widely used theories in atomic physics [14,3]. The core is described by a set of phase shifts (quantum defects) δ_l in each partial wave, quantifying the departure from pure Coulomb behavior. We consider the *s*-wave scattering case, where δ_0 is the only nonzero phase shift, which describes lithium ($\delta_0 \simeq 0.41\pi$) and helium ($\delta_0 \simeq 0.3\pi$ for triplet and $\delta_0 \simeq 0.14\pi$ for singlet helium) extremely well.
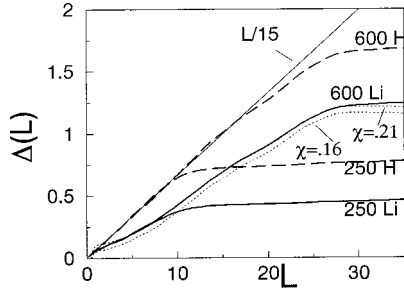
FIG. 1. Rigidities calculated from quantal spectra of hydrogen (H) and lithiumlike (Li) atoms at $\epsilon = -3$ for two different values $\kappa = 250$ and 600 (i.e., effective $\hbar^{-1} = 250\ 600$). The values of κ are indicated on the graphs. The straight line indicates the $L/15$ Poisson limit. The figure shows that the nonhydrogenic rigidities follow a significantly different curve. Surprisingly, given the $\hbar$ dependent nature of the diffractive process, the perturbed curves are essentially independent of $\hbar$ below the saturation value of $L \sim L_{\max}$. The curves from our final semiclassical formula, [Eq. (9)], using either the semiclassical value of the constant shift ($\chi = 0.16$) or the corresponding quantum ($\chi = 0.21$) value, are superimposed on the $\kappa = 600$ nonhydrogenic quantal rigidity, showing the excellent agreement and the relatively modest effect of the uncertainty in the shift χ.

The insertion of a single scattering channel can be represented as a perturbation by a projection operator. In this case, it has been shown [1,8,9,12] that the eigenvalues of the perturbed system remain trapped between the unperturbed eigenvalues. This trapping puts a strong restriction on perturbations to long-range spectral correlations; indeed, in the limit $\hbar \rightarrow 0$ and $L \rightarrow \infty$, the perturbed spectral rigidity can differ from the unperturbed one by at most some value, bounded by 0 and 2.

We have calculated the lowest 36 000 states of the Stark spectrum for magnetic quantum numbers $m = 0$ and $\epsilon = -3$ and a range of quantum defects. The results for $\delta_0 = 0$ (hydrogen) and $\delta_0 = \pi/2$ (''lithium'') for values of the effective $\hbar^{-1}$, $\kappa < 600$, are shown in Fig. 1. These values span and go well beyond typical experimental values. (the experimental NNS statistics [2] correspond to $\kappa \sim 130$–150). Figure 1 shows that for our $\kappa < 600$ range, deviations from Poissonian or hydrogenic ($\delta_0 = 0$) behavior are substantial. Even for such small values of the effective $\hbar$, however, it is evident that the perturbed curves are not obtained by a simple constant shift.

The electronic core yields a combination of Coulomb and s-wave scattering. The Coulomb scattering generates Gutzwiller periodic orbits (PO's): *geometric orbits*. The effect of the s-wave (δ_0) scattering is to generate *diffractive* trajectories $O(\sqrt{\hbar})$ in amplitude weaker than isolated geometric PO's. For atomic core scattering, orbits which close at the nucleus correspond to either periodic or half-periodic orbits: hence—for chaotic or regular dynamics—every diffractive orbit resulting from a single scattering is paired with a geometric periodic orbit or a half-periodic orbit of the same action. In the Stark case there are no half-period contributions; in the magnetic field case there are half-period diffractive contributions (the D orbits seen in Ref. [7]). All multiple scattering diffractive orbits can likewise be associated with a given combination of geometric periodic or half-periodic or-
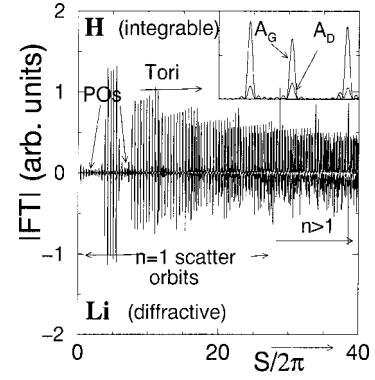

FIG. 2. Amplitudes of Fourier transforms (FT) of scaled spectra plotted against scaled actions $S/2\pi$ for hydrogen and a lithiumlike atom for $\epsilon = -3$. The results are from a fully quantal calculation. S and ϵ are in atomic units. The figure illustrates the relative importance of integrable tori, isolated PO's, and diffractive orbits in different regimes. In the nonhydrogenic atom, for S not too large, one-scatter $n = 1$ diffractive orbits are dominant while the amplitudes of multiple-scattering $n > 1$ diffractive orbits $O(\hbar^{n/2})$ are relatively weak. In the very large S regime [$L \sim O(1)$], however, the proliferation in the number of n- scatter orbits with increasing action means that the $n > 1$ contribution becomes important. The inset amplifies the region around $S \sim 17$. The amplitudes of the diffractive orbits can obtained from the (complex) difference of the hydrogen and lithium traces.

bits. In contrast, in billiard systems diffractive orbits are generally unrelated to the geometric periodic orbits. Their proliferation relative to geometric orbits in the chaotic regime is not restricted by this ''pairing.'' This results in a nonvanishing semiclassical contribution [17].

For integrable atomic spectra, the geometric contribution to the staircase function $\mathcal{N}_G(\kappa) = \mathcal{N}_G^s(\kappa) + \mathcal{N}_G^{osc}(\kappa)$ includes a sum over contributions [18] from integrable tori. In the scaled atomic spectra, $\mathcal{N}_G^{osc}(\kappa) \sim \sqrt{\kappa} \Sigma_j (\mathcal{A}_j/T_j) e^{i(S_j \kappa - \alpha_j \pi/2)}$ The amplitudes $\mathcal{A}_j$ are the Berry-Tabor amplitudes for resonant tori which, in action angle variables, an $\mathcal{A}_j = \sqrt{2\pi/|\boldsymbol{\omega} \cdot \partial \boldsymbol{I}_j / \partial T_j| \mathrm{Det}\{\partial \boldsymbol{\theta}/\partial \boldsymbol{I}_j\}}$.

All tori contain just one PO that collides with the nucleus. Trajectories that can diffract are therefore isolated in the usual sense. The amplitude A_D of the contribution of a particular single-scatter isolated diffractive trajectory of action S, in our 2D system, was given in [7] $A_D^j = S_j / \pi \sqrt{2\pi/m_{12}\kappa} \sin \delta_0 e^{i\delta_0} \sin \phi$, where m_{12} is an element of the reduced monodromy matrix $\mathbf{M}$, and ϕ is the angle of incidence of the orbit relative to the field direction. In integrable systems, $m_{12} \propto S$. Hence A_D scales as $\sqrt{S/\kappa}$. We investigate the ratio of the diffractive to corresponding geometric contribution, $A_D^j / A_G^j = A_D T_j / (\kappa \mathcal{A}_j)$ which we write as $A_D^j / A_G^j = i C_j \sin \delta_0 e^{i\delta_0} S_j / \kappa$. By a unitary transform to action angle coordinates we can show [16] that $C_j \sim \omega_1^{(j)} \omega_2^{(j)}$, where the ω are the frequencies of motion along the two independent degrees of freedom. Hence C_j are independent of κ and do not scale with orbit length. They are nearly constant and fluctuate weakly about an average value [16].

From the Fourier transforms of scaled spectra (see, e.g., Fig. 2), we can confirm this behavior. The A_D / A_G ratios and hence the C_j statistics are obtained numerically from the first ~ 50 pairs.
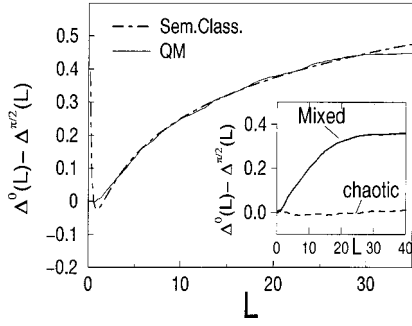
FIG. 3. Comparison between the quantum mechanical (QM) result from numerical diagonalization and the semiclassical (Sem.Class) result from Eq. (9) for the integrable case of atoms in electric fields for a scaled field $\epsilon = -3$ for $\kappa \sim 600$ and $\chi = 0.21$. In order to expose the approximately logarithmic nature of the diffractive correction, here we plot the *difference* between the hydrogenic and diffractive rigidities. The inset shows the corresponding (quantal) results for atoms in magnetic fields for the near-integrable and mixed case (solid line, $\epsilon = -0.6$ and $\kappa \sim 150$) which is qualitatively similar to the integrable case and the fully chaotic rigidity differences (dotted line, $\epsilon = -0.1$, and $\kappa \sim 125$) which are ~ 0.

Since the ratio of the one-scatter diffractive orbits to the resonant tori contributions is $O(S/\kappa)$, which in the unscaled spectra is $O(\hbar T)$, on classical time scales diffraction has a very small effect, but on quantum time scales ($T \sim 1/\hbar$) both contributions are of the same order. We show that a semiclassical analysis of the rigidity is sufficient to reproduce such essentially quantum phenomena.

We have also calculated the lowest 10 000 states of the diamagnetic problem $\epsilon = -0.6$ (near integrable), and $\epsilon = -0.1$ (chaotic). The results are in Fig. 3 (inset). In the chaotic case we find almost no perturbation of the hydrogenic result. Isolated hyperbolically unstable orbits contribute like $|2 - \mathrm{Tr}\,\mathbf{M}|^{-1/2}$, which vanishes exponentially with the orbit period. In such a system, m_{12} typically diverges with the same Lyapunov exponent as $\mathrm{Tr}\,\mathbf{M}$. Hence A_D^j/A_G^j is $O(\sqrt{\hbar})$ regardless of trajectory length. Proliferation of diffractive orbits relative to geometric ones is restricted to additional half-period contributions by some orbits, in contrast to the billiard result [17], where any fraction may contribute. We conclude that, in the accessible $\hbar$ range, the diffractive effect remains small for the chaotic atom, but represents a substantial effect in the integrable case, on quantum time scales.

In the KAM system, deviations qualitatively similar in form to the integrable case occur. We do not attempt a rigorous analysis of systems with a mixed classical phase space, but the numerics support the notion that the structure of the Berry-Tabor formula [18] is retained for near-integrable KAM systems [19], and that our analysis could also find application in such systems.

The preceding arguments are of course incomplete for the rigorous development of a semiclassical limit, as we do not consider multiple scattering effects such as the creation of the *combination orbits*. However, we will see that in the numerically accessible regime (and indeed far beyond experimental resolution) it is not necessary to consider such effects to accurately reproduce the diffractive corrections to the spectral statistics for $L \gtrsim O(1)$, up to a small constant correction.

We now analyze the case of a nonhydrogenic Stark atom. Since we will only be interested in long orbits, for which the uniformity principle [20] can be invoked to connect period with action, we can write the Berry-Tabor formula as a sum over all periodic orbits j (including retracing to negative time) in the form

$$\mathcal{N}_G^{\mathrm{osc}}(\kappa) = -i\kappa^{3/2} \frac{\Delta_\epsilon}{\Delta_\kappa} \sum_j \frac{A_j}{S_j} e^{i(S_j\kappa - \alpha_j\pi/2)}. \qquad (2)$$

Here S_j and α_j, are the scaled action and the Maslov index, A_j is the scaled amplitude factor from Ref. [18], $\Delta_\kappa^{-1} = \partial\mathcal{N}^s/\partial\kappa|_\epsilon$, and $\Delta_\epsilon^{-1} = \partial\mathcal{N}^s/\partial\epsilon|_\kappa$. Note that $\Delta_\kappa/\Delta_\epsilon$ scales as κ.

The contribution to the spectral staircase from the corresponding single-scatter diffractive periodic orbits yields a sum over the same set of periodic orbits as in Eq. (2):

$$\mathcal{N}_D^{\mathrm{osc}}(\kappa) = \sin\delta_0 \sqrt{\kappa} \frac{\Delta_\epsilon}{\Delta_\kappa} \sum_j C_j A_j e^{i(S_j\kappa - \alpha_j\pi/2 \pm \delta_0)}, \qquad (3)$$

where the phase shift $\pm\delta_0$ is positive for forward time tracings, and negative for negative time retracings.

The rigidity formula (1), which is easily adapted for the problem in hand where the *levels* are κ_i, leads to integrals involving the products $\langle\mathcal{N}_G\mathcal{N}_G\rangle_\kappa$, $\langle\mathcal{N}_G\mathcal{N}_D\rangle_\kappa$, and $\langle\mathcal{N}_D\mathcal{N}_D\rangle_\kappa$. These products involve many rapidly oscillating terms, which, following Berry [13], we assume to vanish upon averaging. This approximation is usually known as the *diagonal approximation*, but here we retain different (off-diagonal) trajectories with identical action, which occur due to diffraction.

The resulting equation for the rigidity can be written

$$\Delta^{\delta_0}(L, L_c) = L/15 + \Delta^{DG}(L, L_c) + \Delta^{DD}(L, L_c), \qquad (4)$$

where

$$\Delta^{DG}(L, L_c) = -4\kappa^2 \sin^2\delta_0 \left(\frac{\Delta_\epsilon}{\Delta_\kappa}\right)^2$$
$$\times \sum_j^+ C_j \int_0^{2\pi/\Delta_\kappa L_c} dS(A_j^2/S)$$
$$\times \delta(S - S_j)G(\Delta_\kappa LS/2), \qquad (5)$$

$$\Delta^{DD}(L, L_c) = 2\kappa \sin^2\delta_0 \left(\frac{\Delta_\epsilon}{\Delta_\kappa}\right)^2$$
$$\times \sum_j^+ C_j^2 \int_0^{2\pi/\Delta_\kappa L_c} dSA_j^2$$
$$\times \delta(S - S_j)G(\Delta_\kappa LS/2); \qquad (6)$$

the sum is now only over positive traversals, and $G(y) = 1 - F^2(y) - 3[F'(y)]^2$ $[F(y) = \sin y/y]$ is Berry's *orbit selection function*, which is similar to the step function $\Theta(y - \pi)$. We have had to introduce an upper cutoff to the integrals, which will be seen to diverge. This divergence is a direct result of neglecting the rapidly oscillating terms, and will be discussed further below. We now concentrate on evaluating the integrands of Eqs. (5) and (6). For long orbits,

we invoke the Hannay–Ozorio de Almeida sum rule [20], which can be expressed as $\lim_{S\to\infty}\Sigma_j A_j^2 \delta(S-S_j) = (\Delta_\kappa/\Delta_\epsilon^2)/2\pi\kappa^3$, which is independent of κ. We consider this to be accurate for $S>S^*$, so that our result for Eq. (4) will only be accurate for $L<L_{max}=2\pi/\Delta_\kappa S^*$. Indeed L_{max} also marks the onset of nonuniversal deviations of the non-diffractive result from the simple $L/15$ dependence [13]. Inserting the sum rule into Eqs. (5) and (6), averaging over the distribution of C_j and evaluating the integrals, leads to closed form solutions that can be expressed in terms of special functions [16]. Here we only write out the asymptotic approximations to the solutions:

$$\Delta^{DG}(L,L_c)\sim -\frac{2\langle C_j\rangle\sin^2\delta_0}{\pi\kappa\Delta_\kappa}\left[\ln\frac{2\pi L}{L_c}+\gamma_E-\frac{9}{4}\right], \quad (7)$$

$$\Delta^{DD}(L,L_c)\sim \frac{2\langle C_j^2\rangle\sin^2\delta_0}{\kappa^2\Delta_\kappa^2}[L_c^{-1}-L^{-1}], \quad (8)$$

where γ_E is Euler's constant. $\kappa\Delta_\kappa$ is a constant, independent of κ, and $\sim -2\epsilon$ for our Stark spectra. The result is valid for $L>L_c$, and the ambiguity in L_c leads to an ambiguity in the constant term. For $L\ll L_c$ both Δ^{DD} and Δ^{DG} vanish. To proceed, one should invoke the semiclassical sum rule due to Berry [13]. It is natural then to identify L_c as $2\pi/\Delta_\kappa S_c$, (e.g., $L_c\sim 0.94$ for the case in Fig. 3), where S_c is the point where the semiclassical and quantum asymptotes for the form factor coincide. Since we have neglected both off-diagonal corrections and higher order scattering contributions, we cannot expect to be able to evaluate the constant term correctly. In this case we can simply set L_c to unity, and accept that our result may not be accurate around $L\simeq 1$. We note that in the Gaussian orthogonal ensemble case it is also not possible to evaluate the constant term semiclassically [13].

The final result for the rigidity is then

$$\Delta^{\delta_0}(L)=\Delta^0(L)+\frac{\sin^2\delta_0}{\epsilon}\left[\frac{\langle C_j\rangle}{\pi}\ln L-\frac{\langle C_j^2\rangle}{2\epsilon L}\right]+\chi \quad (9)$$

for $L_{max}\gtrsim L\gtrsim 1$, where χ is the constant shift. For $L\lesssim 1$, $\Delta^{\delta_0}(L)=L/15$. The final formula hence does not contain the effective Planck's constant, proving the most surprising feature of Fig. 1, namely, that despite the $\hbar$-dependent nature of the diffractive corrections, our quantal results (below L_{max}) are essentially $\hbar$ independent.

We find $\langle C_j\rangle\simeq 1.8$, and $\langle C_j^2\rangle\simeq\langle C_j\rangle^2$ for the $\epsilon=-3$ case. We stress that these were not free parameters. With $L_c\sim 1$ from Eqs. (7) and (8) we find $\chi\sim 0.16$ for $\delta_0=\pi/2$. However, we estimate from the quantal results that $\chi\sim 0.21$. The correction required can be attributed to the neglect of both higher order scattering and off-diagonal contributions.

Our result is compared with the fully quantal values shown in Fig. 1, and the quantal and semiclassical rigidities are plotted in Fig. 3. The agreement (to within the small correction to χ) is extremely good up to L_{max}, where the breakdown was expected. The divergent nature of Eq. (9) for $L<1$ is clearly seen. The $\sin^2\delta_0$ dependence has been verified by considering several different defect values (not shown) [16].

To summarize, we have combined the semiclassical theory of diffraction and atomic quantum defect theory with the Berry-Tabor trace formula to give diffractive corrections to the spectral rigidity of atoms in fields. We show that within a small constant shift, the semiclassical one-scatter results agree extremely accurately with the fully quantal results.

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